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010871964 **Image available**
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Preventing slime formation in paper making processing water - by adding N-halo- or N,N-dihalo-hydantoin cpd. as antifungal agent effective at low or high pH

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Number of Countries: 001 Number of Patents: 001
Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Week	
JP 8176996	A	19960709	JP 94322939	A	19941226	199637	B

Priority Applications (No Type Date): JP 94322939 A 19941226
Patent Details:

Patent No	Kind	Lan	Pg	Main IPC	Filing Notes
JP 8176996	A		7	D21H-021/04	

Abstract (Basic): JP 8176996 A

Prevention of slime problems in a pulping or paper making factory involves adding an N-halo-hydantoin cpd. of formula (I) to the processing water used in the factory, to sterilise slime-forming fungi or prevent their growth. In (I), one of R1 and R2 are Cl or Br and the other is H, Cl or Br; and R3 and R4 are H or 1-12C alkyl.

USE - Esp. used for treating white water released from alkaline paper making machine.

ADVANTAGE - Effect is sufficient in processing water having a pH of 4-6 or a pH of 6-8.

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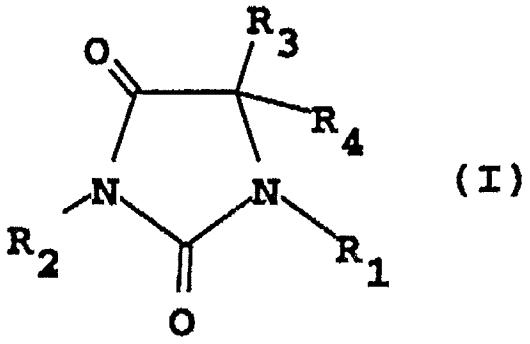


(I)

Title Terms: PREVENT; SLIME; FORMATION; PAPER; PROCESS; WATER; ADD; N; HALO ; N; N; DI; HALO; HYDANTOIN; COMPOUND; ANTIFUNGAL; AGENT; EFFECT; LOW; HIGH; PH
Derwent Class: C02; D15; E13; F09
International Patent Class (Main): D21H-021/04
International Patent Class (Additional): A01N-043/50; C02F-001/50
File Segment: CPI
Manual Codes (CPI/A-N): C07-D09; C14-A06; C14-B15; C14-W; D04-A01P; D04-A02 ; E07-D09D; F05-A02B
Chemical Fragment Codes (M2):
01 C017 C035 F011 F012 F013 F014 F015 F017 F523 H2 H211 H212 J5 J522 K0 K1 K130 K199 L9 L910 M210 M211 M212 M213 M214 M215 M216 M220 M221 M222 M223 M224 M225 M226 M231 M232 M233 M240 M280 M281 M282 M320 M413 M510 M521 M530 M540 M781 M903 M904 P241 Q231 9637-66201-U
Chemical Fragment Codes (M3):
01 C017 C035 F011 F012 F013 F014 F015 F017 F523 H2 H211 H212 J5 J522 K0 K1 K130 K199 L9 L910 M210 M211 M212 M213 M214 M215 M216 M220 M221 M222 M223 M224 M225 M226 M231 M232 M233 M240 M280 M281 M282 M320 M413 M510 M521 M530 M540 M781 M903 M904 P241 Q231 9637-66201-U
Generic Compound Numbers: 9637-66201-U

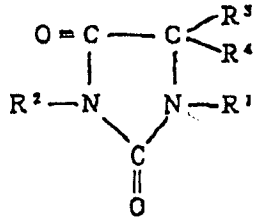
Japanese Patent 08176096, 1994

Translation of Japanese Patent into English.

[What is claimed.]

[Claim 1]

Slime controlling method using hydantoin compound with following structure (1) by killing or inhibiting the growth of microbe which forms slime in the process water of paper & pulp mills.



Structure (1)

(wherein R_1 and R_2 are same or not, one is chlorine or bromine and the other is hydrogen, chlorine or bromine. R_3 and R_4 are same or not, and each of them are hydrogen or alkyl groups of C_1 - C_{14}.)

[Claim 2]

Slime controlling method described in Claim 1. The process water is white water exhausted from paper-making machines which are operated in alkali condition.

[Claim 3]

Slime Controlling methods described in Claim 1 and 2. In the structure (1) of hydantoins, R_1 or R_2 is chlorine or bromine, and R_3 and R_4 are methyl group.

[Detailed description of the invention.]

[0001]

[Industrial Application]

It is the object of the present invention to prevent the slime troubles in the process water of paper & pulp mills.

[0002]

[Background of the invention]

It is widely known that the increase of microbes in the water used in the process of paper & pulp mills cause many troubles. White water exhausted from paper-making machines is a very good condition for bacteria to increase because it contains pulps which can be nutrient sources for microbes, and it also contains many chemicals and fillings.

Furthermore the temperature of the water is good for increase of microbes. After bacteria increase in white water, bacteria and the metabolites coagulate and yield slimy materials called slime. When slime grows to a considerable size, it comes off due to water flow speed, mix with paper and damages them by providing stain, spot and eye spot. In addition, it causes paper cutting, clog of wire and blanket, corrosion and stink. As a result, it makes serious problems in the the operation. As the water in the process contacts papers directly and the part of the water is taken in the papers, slime problem in the process water is more serious than that in the cooling water.

[0003]

There are some methods to make paper, such as acid based process co-using sizing agent, sulfuric acid band as stabilizers, and alkali based process using calcium carbonate as a filler. The acid based process in the pH range of 4 - 6 was traditionally popular, but recently alkali based is getting common. The advantage in alkali based process is to make white water closed and utilize cheap calcium carbonate as a filler. The disadvantage in this process is to increase the water temperature in closed system, concentrate the nutrient and make the microbes adhere to filler. It offers the comfortable living environment to bacterial. In addition, pH range of 6 - 8 is most appropriate to form the slime. Conclusively, alkali based process is much better environment to form and grow slime than acid based. On the other hand, the recycle of used paper is paid attention to from the ecological point of view such as the protection of forest resource and is increasing year by year. However, many kinds and amounts of chemicals are added to recycle used papers to raise the quality and yield of paper. It makes contaminated situation easily in this system.

[0004]

Many kinds of biocides are traditionally used to prevent the growth of microbe and subsequent the occurrence of slime in paper & pulp industry. For instance, organic bromine compounds such as 2,2-dibromo-3-nitrilopropionamid and 1,4-bisbromoacetoxy-2-butene, isothiazolone such as 5-chloro-2-methyl-4-isothiazolon-3-one or 2-methyl-4-isothiazolon-3-one and α-chloro benzaldoxim (JP H6-49797). The operation in paper & pulp industry has recently been changing from social and economic reasons such as developing paper making process or increase of recycling of used papers, and consequently the slime trouble has been diversified and complex. In such a situation, traditional biocides are not sufficient to meet the requirement from the industry to demand much more improved biocide. The traditional biocides are known to be considerably effective against microbes, but to make microbe easily biocide-resistant in acid based process.

A large amount of biocides must be added to maintain or raise the efficacy. It is not practical economically. These biocides shows low microbiological efficacy in alkali based process since they were initially developed to be used in acid based process. It is desire to develop the biocide which can provide the stable efficacy in both acid and alkali based process.

[0005]

[What is the problems?]

As described above, the purpose of the present invention is to introduce new slime controlling agent to paper & pulp industry where requires the microbiological performance available in new serious environment.

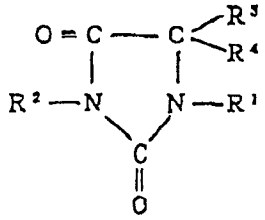
[0006]

[How to solve the problems?]

We took into account the problem described above such as in the condition in alkali based process or increase of recycling of used papers, and studied hard to solve them. Consequently, we could find out the method to prevent the growth of microbes forming slime or kill them with a specific hydantoin compound fed at low level in process water and without any damage to paper, whatever the process is.

[0007]

Structure (1)



This invention is a method to prevent the trouble of slime by feeding the hydantoin compound of above structure (wherein R_1 and R_2 are same or not, at least one is chlorine or bromine and another is hydrogen, chlorine or bromine. R_3 and R_4 are same or not, and each of them is hydrogen or alkyl group of C_1 - C_{12}.) It has the characteristic to kill slim forming microbe or prevent its growth.

[0008]

In formula (1) described above, R_1 and R_2 are same or not, at least one is chlorine or bromine and another is hydrogen, chlorine or bromine. R_3 and R_4 are same or not, and each of them is hydrogen or alkyl group of C_1 - C_{12}, preferably C_1 - C_4. Alkyl group of C_1 - C_{12} is methyl, ethyl, n-propyl, isopropyl, n-butyl, n-hexyl, 2-ethylhexyl, n-octyl, or n-dodecyl.

The alkyl group of more than C_{13} is not preferable because it lowers water solubility extremely. Hydantoin compound described in above formula (1) is 1-bromo-3-chloro-5, 5-dimethylhydantoin, 1, 3-dibromo-5, 5-diethylhydantoin, 1, 3-dibromo-5-5-butylhydantoin or 1, 3-dichloro-5,5-dimethyl hydantoin.

[0009]

In the present invention, the process water in paper & pulp mills includes not only so called white water which is exhausted from wood crushing process, paper-making process, screening process, or bleaching process but also all water which is used in all processes of paper & pulp mills.
The feed of hydantoin compound to water process depends on the quality of water, the number of microbe, the frequency of slime occurrence, the kind of hydantoin compound or the feed speed. In general, it is the range of 0.1 to 100 ppm, preferably, 0.5 to 50 ppm, more preferably 1.0 to 20 ppm. The feed of less than 0.1 ppm is slight effective and that of more than 100 ppm is effective enough, but not economically advantageous. The feed of hydantoin compound described above doesn't have any influence to process and not damage the quality of paper.

[0010]

The hydantoin compound used in the present invention is solid at normal temperature and has the water solubility of 0.1 to 0.2 % wt / wt. In general, the powder of hydantoin compound is fed in water, otherwise it is fed after it is dissolved in water. Taking the convenient feed method into account, it is recommended to feed it in each required place in the process with the pump.
It is also possible to feed hydantoin compound dissolved in organic solvents compatible with water such as acetone, dioxane, dimethylformamide or N-methylpyrolidone. Such solvents may be the nutriment to microbes. Therefore, it is not recommendable to use the organic solvents because they will be nutrient source for mickrobe. When it is used in the solution of water or organic solvent, it is recommendable to feed it immediately in the process after dissolved, from the point of view of stability. There are feed systems in water, not specified, such as shock feed at regular interval in the high concentration, the slug feed or continuous feed to maintain the regular concentration. Anyhow, it should be fed to maintain the number of microbes to less than specific level and subsequently, inhibit the slime trouble.

[0011]

[Practice] This invention is hereinafter explained in the details.

Practice 1 - We selected gram negative bacterial Pseudomonas. sp and gram positive bacteria Bacillus. sp as a sample microbe which is represented in white water in paper & pulp mills, and cultivated each one at the temperature 32℃ in TGY liquid culture (pH 7.0) for 24 hours.

The liquid culture is diluted to 100 times in sterilized water and made the suspension of each pH 5, 6, 7, 8, 9. The biocide of concentration 10 ppm is added to the suspension 100 ml in 300 ml flask and mixed for 0.5 hours in the shaker. After the mixture is inoculated to TGY agar culture and cultivated at 32℃ for 3 days, the number of bacteria per white water 1 ml is counted.

The test result is illustrated together the comparable biocide in Table 1. It is clear from Table that hydantoin compound can reduce the number of bacteria sharply as compared with another biocide, the difference is especially remarkable in alkali pH range.

[0012]

[Table 1]

Slime Control Agent	Bacteria	Number of Bacteria (number / ml)				
		pH				
		5	6	7	8	9
1-bromo-3-chloro-5,5 dimethyl hydantoin	Pseudomonus	$1x10^2$	$2x10^2$	$2x10^3$	$8x10^2$	$5x10^2$
	Bacillus	$1x10^3$	$1x10^3$	$5x10^3$	$4x10^2$	$7x10^2$
Comparison						
2-dibromo-3-nitrilo propionamide	Pseudomonus	$5x10^4$	$1x10^4$	$9x10^5$	$5x10^5$	$4x10^6$
	Bacillus	$3x10^4$	$9x10^4$	$1x10^5$	$5x10^5$	$6x10^6$

[0013]

Practice 2 - White water (pH 5.4, number of bacteria 2 x 10^7/ml) 100 ml in acidic paper-making machine is sampled in 300ml flasks, and biocide of concentration 0.1, 1, 10, 30, 100 ppm is added and mixed in the shaker for 0.5 and 1 hour. After each mixture is inoculated to TGY agar culture and cultivated at 32℃ for 3 days, the number of bacteria per white water 1 ml is counted.

This test result is illustrated together with comparable biocides in Table 2. It is clear from Table that hydantoin compound can reduce the number of bacteria sharply as compared with other biocides.

[0014]

[Table 2]

	Slime Controlling Agent	Feed (ppm)	Number of Bacteria (number / ml) 0.5 hour	1 hour
Examples				
1		0.1	$1x10^5$	$7x10^3$
2	1,3-dibromo5.5-	1	$1x10^4$	$2x10^3$
3	diethylhydantoin	10	$1x10^5$	<10
4		30	$5x10^7$	<10
5		100	<10	<10
6		0.1	$3x10^3$	$2x10^4$
7	1-bromo-3-chloro-5,5	1	$9x10^3$	$8x10^3$
8	dimethylhydantoin	10	$1x10^3$	<10
9		100	<10	<10
10	1.3-dibromo 5-methyl	0.1	$4x10^5$	$2x10^3$
11	5-ethylhydantoin	10	$2x10^3$	<10
12		30	$7x10^2$	<10
Comparison				
1		0.1	$2x10^7$	$9x10^5$
2	2-dibromo	1	$9x10^5$	$8x10^5$
3	3-nitrilopropinamide	10	$5x10^5$	$5x10^3$
4		30	$1x10^6$	$2x10^4$
5		100	$8x10^6$	$1x10^4$
6	Methylene bisthiocyanate	1	$2x10^7$	$2x10^7$
7		10	$2x10^7$	$1x10^7$
8		100	$8x10^6$	$9x10^6$
9	2-bromo-2-nitropropane-	1	$9x10^8$	$1x10^7$
10	1,3-diol	30	$1x10^7$	$5x10^6$
12		100	$2x10^7$	$7x10^6$
13	1.4-bisbromoacetoxy	1	$1x10^7$	$1x10^7$
14	2-butene	100	$2x10^7$	$9x10^6$
15	5-chloro2-methyl-4- iso	0.1	$1x10^7$	$1x10^7$
16	thiazolone-3-one/2-methyl-	1	$1x10^7$	$7x10^6$
17	4-isothiazolon-3-one	10	$9x10^6$	$5x10^6$
18	(weight rate 1:1)	100	$9x10^6$	$9x10^5$

[0015]

Practical 3 - White water (pH8.0 number of bacteria $1x10^9$/ml) from alkali paper-making machine in paper mill was tested in the same method as Practice 2. The result is in table 3 with comparisons. When the hydantoins were used, the number of bacteria decreased more sharply than when the comparable samples were used. Especially the difference is more remarkable in white water from alkali based paper- making machine than from acidic based.

[0016]

[Table 3]

	Slime controlling agent	Concentration (ppm)	Number of Bacteria (number / ml) 0.5 hour	1 hour
Hydantoins				
1		0.1	$1x10^5$	$3x10^5$
2	1,3-dibromo-5.5-	1	$1x10^2$	<10
3	diethylhydantoin	10	$1x10^2$	<10
4		30	<10	<10
5		100	<10	<10
6		0.1	$5x10^5$	$1x10^5$
7	1-bromo-3-chloro-5,5-	1	$4x10^2$	<10
8	dimethylhydantoin	10	$6x10^2$	<10
9		100	<10	<10
10	1,3-dibromo- 5,5-dipropyl	0.1	$1x10^5$	$1x10^5$
11	hydantoin	10	$7x10^2$	<10
12		30	$7x10^2$	<10
13		0.1	$2x10^5$	$4x10^3$
14	1,3-dichloro-5-ethyl-5-	1	$9x10^2$	<10
15	butylhydantoin	10	$5x10^2$	<10
16		30	$1x10^2$	<10
17		100	<10	<10
1		1	$1x10^9$	$2x10^5$
2	2-dibromo	10	$1x10^9$	$1x10^7$
3	3-nitrilopropinamide	30	$1x10^9$	$2x10^8$
4		100	$9x10^9$	$8x10^4$

5		1	$9x10^9$	$1x10^9$
6	Methlenebisthiocyanate	30	$1x10^9$	$5x10^8$
7		100	$2x10^7$	$7x10^8$
8	2-bromo-2-nitropropane-	1	$1x10^9$	$1x10^9$
9	1,3-diol	100	$2x10^3$	$9x10^8$
10		0.1	$1x10^9$	$1x10^9$
12	1,4-bisbromoacetoxy-	1	$1x10^9$	$7x10^7$
13	2-butene	10	$1x10^9$	$5x10^8$
14		100	$8x10^8$	$9x10^8$
15		0.1	$1x10^9$	$6x10^8$
16	5-cloro-2-methyl-4-	1	$9x10^8$	$9x10^7$
17	itothiazolone-3-one /	10	$7x10^8$	$4x10^8$
18	2-methyl-4-isothiazolone-	30	$8x10^8$	$2x10^6$
19	3-one (weight=1:1)	100	$8x10^9$	$7x10^5$

[0017]

[Achievement of the invention]

This invention can kill or inhibit the growth of microbes which forms slime in process water of paper & pulp mills. Consequently, it can prevent the slime trouble before it takes place in the process. It is effective enough in both pH ranges of acidic such as 4 - 6 and alkali such as 6 - 8.

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